SPECTROSCOPIA MOLECULAR

Un bulletin mensual de novas e informationes de interesse e valor al spectroscopistas molecular

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TRACTAMENTO DEL COORDINATAS NORMAL DE MOLECULAS POLYATOMIC

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(Traducite e redigite per Forrest F. Cleveland)
(Recipite le 24 de augusto 1953)

1.0 INTRODUCTION

WILSON[1,2] ha disveloppate un methodo pro obtener le frequentias vibrational de moleculas polyatomic in le qual le theoria de gruppos es usate pro simplificar le calculationes. Le methodo es specialmente bon pro moleculas que ha symmetria considerabile e, ergo, plure atomos equivalente, i.e., atomos con nucleos identic le quales se transforma le unes in le alteres pro omne operationes del gruppo del molecula. Un altere avantage del methodo es que illo usa le cambiamentos in le distantias ligaminic e le angulos interligaminic como coordinatas generalisate, in terminos del quales le constantes del energia potential ha un plus clar significantia physic e pote esser transferite ab un molecula a un molecula similar, al minus a un certe grado de approximation[3].

[1] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

[2] Vide etiam un articulo elementari re iste methodo per A. G. Meister e F. F. Cleveland, Am. J. Phys. 14, 13 (1946).

[3] B. L. Crawford, Jr., e S. R. Brinkley, J. Chem. Phys. 9, 69 (1941).

[4] G. Herzberg, Infrared and Raman Spectra of Polyatomic Moleculas (D. Van Nostrand Company, Inc., New York 1945), prime edition, pagina 140.

Como Herzberg dice[4], le determination del constantes del energia potential es un del objectos principal del studio del structura vibrational del spectros de moleculas polyatomic; isto pote esser viditc solmente si on pote dar un clar significantia physic al constantes del energia potential.

Un numero de disveloppamentos del methodo de Wilson ha essite publicate. De un latere, con le perception que le calculation del elementos del matrice del energia cinetic esseva un del plus tediose passos in le processo, Decius[5] dava un tabulation de tal elementos pro le typos ordinari de coordinatas interne que es usate in le plus grande numero del calculationes. Como indicate per Decius mesme, alicun deficientias occurre in le tabulas; i.e., in le caso de moleculas plan le quales ha nulle catena de atomos ligate con un longitude de quatro atomos, e pro le caso de moleculas que ha un catena de tres o plus atomos collinear. Lohman[6] re-

[5] J. C. Decius, J. Chem. Phys. 16, 1025 (1948).

[6] J. B. Lohman, Reporto Technic del

IE characteristicas principal de education universitari debe esser le disveloppamento de initiativa e originalite in recerca, de un evaluation critic del litteratura e del recerca del studente mesme, del capabilitate de preparar reportos concise e critic, e de facilitate in le presentation oral del resultatos de recerca.

-- E. M. Billings, Chem. and Eng. News 26, 166 (1948).

Bureau de Recerca Naval, No. 17 (1951).
[7]S. M. Ferigle e A. G. Meister, J. Chem. Phys. 19, 982 (1951).

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moveva le prime de iste deficientias e addeva un nove typo de coordinata interne, un que corresponde a un flecto-vibration extraplanar. Le secunde deficientia esseva removite per Ferigle e Meister[7]. Del altere latere, alicun articulos ha essite scribite super le methodo de obtener le coordinatas de symmetria[8-10], le qual esseva al comenciamento un materia de experientia e intuition, e Decius[11] ha date

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[8]T. Venkatarayudu, Proc. Indian Acad.Sci. 17A, 50 (1943).
[9]J. E. Kilpatrick, J. Chem. Phys.16, 749 (1948).
[10]J. R. Nielsen e L. H. Berryman, J. Chem. Phys. 17, 659 (1949).
[11]J. C. Decius, J. Chem. Phys. 16, 214 (1948).

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un citation a un methodo disveloppate per Lippman pro le factorisation del equation secular.

Finalmente, disveloppamentos ha essite facite pro poner in relation le constantes del energia potential con le structura molecular e a trovar un significantia definite non solmente pro le pur terminos quadratic sed etiam pro le si-appellate constantes de interaction.

Proque le novicio in calculationes de frequentias vibrational trova le symbolismo del articulos de Wilson difficile, e proque altere articulos super le methodo omitte multes del detalios il pare de valor a dar un tractamento elementari de alicun moleculas typic pro illes qui desira comenciar laborar in iste campo. Le molecula H_2O es considerate ante toto proque illo ha solmente un parve numero de atomos, ha nulle frequentias degenerate, e permittite al lector concentrar se super le methodo sin esser confundite per le complexitate del molecula. Tunc le moleculas CH_3Cl, CH_4, e CD_4 es tractate pro demonstrar como le methodo es applicate quando frequentias es presente que es duplemente o triplemente degenerate.

Un nomenclatura systematic essera empleate in iste articulo. Isto es considerate como del plus grande importantia proque nulle passos ha essite facite in iste direction, lo que face le lectura del litteratura in le campo difficile e innecessarimente tediose. Iste nomenclatura se ha provate extrememente usabile in le studio del methanos substituite e altere typos de moleculas.

2.0 DELINEATION DEL METHODO

Le equation secular es obtenite in duo passos:

(1) In le prime passo, le expression pro le energia potential e le energia vibrational cinetic es obtenite in terminos del coordinatas interne e lor derivativos con respecto al tempore.

Como mentionate supra, le coordinatas interne es seligite de maniera que un significantia physic pote esser date al functiones con le quales illos es associate. Illos es definite secundo le systema de ligatura del qual on suppone que illo existe in le molecula. Decius[12] ha date un description e discussion detal-

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[12]J. C. Decius, J. Chem. Phys. 17, 1315 (1949).

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iate del typos differente de coordinatas interne que es usate in le studio del parve vibrationes de moleculas polyatomic. Isto es classificate in quatro typos:

(a) Tension del ligamine. Illo es definite como le differentia del distantia internucleari inter le duo atomos que es directemente ligate in le configuration distorquite e le distantia internucleari inter le mesme duo atomos in le configuration de equilibrio.

(b) Flection interligaminic. Illo es definite como le differentia inter le angulo que es formate per duo ligamines adjacente in le configuration distorquite e le correspondente angulo in le configuration de equilibrio.

(c) Flection extra le plano. Illo es definite pro un gruppo de tres atomos omnes del quales es ligate a un quarte atomo. Illo es le cambiamento in le angulo formate per le plano del tres atomos e le ligamine del altere atomo con le un que es in commun.

(d) Torsion del ligamine. Illo es definite ubique atomos a cata fin de un ligamine (o un numero de ligamines collinear) es etiam ligate cata un a atomos additional per ligamines que non es collinear con le ligamines que connecte le duo atomos in question. Le duo atomos terminal prendite respectivemente con le ligamine o ligamines de connexion defini duo planos; le coordinata de torsion interne es definite como le cambiamento in le angulo dihedre inter le duo planos.

Iste quatro typos de coordinatas interne es sufficiente pro describer omne le grados de libertate, vibrational, como Decius[12] lo ha demonstrate; i.e., il es semper possibile trovar pro alicun molecula de N atomos 3N - 6 coordinatas appropriate del supra-mentionate typos que es independente e pote esser usate pro describer le vibrationes molecular.

(2) In le secunde passo, le proprietates de symmetria del molecula es usate. Le si-appellate coordinatas de symmetria es obtenite. Istos es combinationes linear del coordinates interne. Il es convenibile construer le coordinatas de symmetria ex solmente ille coordinatas interne que es equivalente. In plus, le selection del combinationes linear non es arbitrari sed debe esser facite in un tal maniera que le coordinata de symmetria se transforma secundo le characteres pro le typo de vibration que es concernite. Etiam, le coordinatas de symmetria debe esser orthogonal e normalisate. Iste transformation duce a un factorisation complete del equation secular le qual es possibile a causa del invariabilitate del energias cinetic e potential sub omne le operationes del gruppo del molecula.

(Va continuar in un numero futur.)

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DUO PERIODICOS NON-SPECTROSCOPIC

FORSAN alicunes del lectores habera un interesse in le un o le altere de duo nove periodicos. Istos es:

(1) PEN-PRINTS. Isto es un publication international pro uso in le homes e scholas a transverso del mundo. Le objectivo de illo es jocar un parte in le designo gigantesc del pace del mundo per assister le populos del mundo a comprehender se le unes le alteres in un melior maniera per le participation in interesses e traditiones commun. De plus, le objectivo de illo es extender se al infantes, ubique possibile, con un message de amor e comprehension e un portrait sympathic de omne nationalitates.

Le redactor de iste periodico es seniora Nora Ashman. Le adresse es: PEN-PRINTS, INC., Cassa postal 125, Indianapolis, Indiana, Statos Unite. Le precio de un abonamento es $1.00 pro duo numeros per anno.

(2) NOVAS DE INTERCAMBIO MUNDIAL. Iste es un periodico dedicate al popularisation e uso mundial de Interlingua inter mercatores e collectores al proposito de un melior intercambio de ideas e cosas philatelic e altere. Illo es publicate per senior Kirtland Harsch, 930 Highland Rd., Birmingham 9, Alabama, Statos Unite.

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NOVE LIBROS

Chimia Quantic. Per Kenneth S. Pitzner. Prentice-Hall, 70 Fifth Avenue, New York 11; 1953. 529 + x Paginas; appendices, 24; indices de autores e de materias. In anglese. Precio, $10.00.

ISTE LIBRO se adressa al chimista physic. Illo pote esser comprendite per un lector qui ha completate le cursos general in calculo, physica, e chimia physic, e qui ha obtenite un pauco de familiaritate con thermodynamica chimic e con le resultatos experimental de physica atomic. Le structura fundamental del theoria del quantos, e alicun applicationes illustrative, es date in le texto. Materias plus mathematic es reservate pro le grande numero de appendices.

Subjectos tractate es: statos stationari, elementos del mechanica de undas, le atomo hydrogenic e le molecula diatomic, proprietates del functiones undic, atomos polyelectronic, theoria de radiation, theoria cinetic e statistica, ligamines chimic e valentia, spectros molecular e proprietates thermodynamic de gases perfecte, solidos crystallin, gases imperfecte e liquidos, phenomenos nucleari, e altere topicos.

Problemas e citationes general es date al fin de cata capitulo. Le ben-cognoscite autor ha publicate un grande numero de articulos super topicos chimic theoric. Un Guida Simple al Theoria Moderne de

Valentia. Per G. I. Brown, con un prefacio per L. E. Sutton. Longmans, Green and Company; London, New York, Toronto; 1953. Paginas, 175 + x, un appendice, e un indice. In anglese. Precio, $2.50.

ISTO ES UN tractamento intermediari que es situate in le region inter le tractamentos de valentia date in le libros standard de chimia e le monographias plus avantiate super valentia. Illo es planiate pro studentes in le prime anno del universitate e pro le lector general qui ha un interesse in le disveloppamentos moderne in iste campo. Le tractamento es simple, concise, e principalmente qualitative. Considerationes mathematic e detalios experimental ha essite reducite al minimo.

Topicos discutite es: un delineation del structura atomic; le arrangiamento del electrones extra-nucleari in un atomo; ligamines de valentia; ligamines electrovalente, covalente, e dative; methodos experimental; dimensiones interne de crystallos e moleculas; exemplos simple de moleculas resonate; hydrogeno e le ligamine hydrogenic; e orbitales molecular.

Il pare que iste monographia elementari pote formar un introduction excellente al subjecto de valentia.

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NOVAS E COMMENTOS

LE DEPARTIMENTO de physica del Tennessee A. and I. State University (Nashville 8, Tenn.) desira annunciar le disponibilitate del facilitates de su laboratorio de spectroscopia infrarubie al laboratorios de recerca chimic del universitates e industrias in le region del sud-est del Statos Unite. Pro plus detalios, scribe a Dr. James R. Lawson.

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DR. DUSAN HADZI (Kemicni Institut, Slovenska Akademija, Ljubljana, Yugoslavia) desira exprimer su gratias a omne le spectroscopistas que inviate a ille reimpressiones de lor articulos super spectros molecular. Altere reimpressiones essera appreciate.

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CON LE MORTE de Dr. K. W. F. Kohlrausch in Graz, Austria, al 17 de Septembre 1953, le spectroscopia molecular ha perdite un de su scientistas le plus ben-cognoscite. Pro un grande numero de annos, professor Kohlrausch esseva le chef del Physikalisches Institut der Technischen Hochschule in Graz, e ha publicate plure libros e proxime a 200 articulos super spectroscopia Raman. Le spectroscopia molecular, e in particular le spectroscopia Raman, ha perdite un de su plus grande amicos. Nonobstante, su labor va viver eternemente in le paginas del litteratura scientific. Illo es un monumento a un del gigantes del spectroscopia.

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UN TRADUCTION IN anglese del articulo russe, "Relationes inter le momentes de inertia e le frequentias de rotation de moleculas isotope", per L. M. Sverdlov, Doklady Akademii Nauk, SSSR, 88, 249 (1953) es disponibile a un precio de $0.10 ab le Office of Technical Services, Washington 25, D. C., Statos Unite.

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(continuate a pagina 52, columna 1)

LONGITUDE DE UNDAS PRO LE CALIBRATION DE SPECTROMETROS PRISMATIC

E. K. PLYLER E C. W. PETERS ha date un tabula de longitudes de undas, e le correspondente numeros de undas corrigite al vacuo, que es de grande valor in le calibration de spectrometros prismatic infrarubie (J. Research Natl. Bur. Standards, 45, 462 (1950)). Infelicemente, il ha alicun errores in le columna del numeros de undas, e Dr. Plyler opina que le publication del correcte valores in iste bulletin esserea un servicio a ille spectroscopistas qui ha un necessitate de un tal tabula.

Le correcte valores es como seque:

Longitudes de undas	Numeros de undas
14,98µ	667,4 K*
13,883	720,1
9,672	1033,6
6,692	1493,9
4,866	2054,5
4,258	2347,9
1,36728	7311,8

*K = kaysers = cm^{-1}.

Omne le altere valores date in le tabula de Plyler e Peters es correcte.

SYMPOSIO SPECTROSCOPIC A NEW ORLEANS

UN SYMPOSIO SUPER le subjecto general, "Application de Spectroscopia al Agricultura e Industria del Sud", essera tenite in connexion con le Juncte Conclave del Regiones del Sud-est e Sud-west del American Chemical Society al Hotel Jung in New Orleans, Louisiana, le 10 al 12 de decembre 1953.

Le symposio includera omne brancas de spectroscopia con un autoritate prominente a presentar un discurso invitate in cata campo. Ben que le detalios non ha essite completate, e un data exacte del symposio ha nondum essite fixate, un convention plen de successo pare assecurate per le recepta de promissas definitive a presentar discursos per le sequente bencognoscite spectroscopistas:

A-1. Spectroisotopos per J.Rand McNally, Jr., Oak Ridge National Laboratory, Cassa postal P, Oak Ridge, Tennessee;

A-2. Spectroscopia Massic per B. W. Thomas, Humble Oil and Refining Company, Departimento de raffinamento, Divisiones Technic e recercic, Baytown, Texas;

A-3. Spectroscopia Emissionic per E. E. Creitz, Statounitesse Bureau de Minas, Cassa Postal L, Universitate Alabama;

A-4. Spectrophotometria Infrarubie per R. C. Gore, Laboratorios de Recerca Stanford, American Cyanamid Company,Stanford, Connecticut.

A-5. Spectroscopia de Fluorescentia Röntgenic per Fred Behr, North American Philips Company, Inc., 750 S. Fulton Avenue, Mt. Vernon, N. Y.; e

A-6. Spectroscopia Raman per Forrest F. Cleveland, Instituto Technologic de Illinois, Chicago 16, Illinois.

Robert T. O'Connor es le chef del symposio de spectroscopia e Leo A. Goldblatt es le chef del committee programmatic. Le adresse de ambes es: Southern Regional Research Laboratory of the U. S. Department of Agriculture, 2100 Robert E. Lee Boulevard, New Orleans, Louisiana.

-- Robert T. O'Connor.

CORRECTIONES A VACUO DEL NUMEROS DE UNDAS

IN UN GRANDE numero de articulos super spectroscopia Raman e infrarubie, le listate numeros de undas correspondente al frequentias vibrational e rotational es referite a aere, non a vacuo. Pro tractamentos theoric, il es necessari que istos es corrigite a vacuo. Un tabula convenibile de tal correctiones es le sequente:

Region	Subtrahe ab σ_{aere} pro obtener σ_{vacuo}
400 - 550 K	0,1 K
551 - 900	0,2
901 - 1250	0,3
1251 - 1600	0,4
1601 - 1950	0,5
1951 - 2400	0,6
2401 - 2800	0,7
2801 - 3200	0,8
3201 - 3500	0,9
3501 - 3850	1,0
3851 - 4150	1,1
4151 - 4450	1,2
4451 - 4800	1,3
4801 - 5200	1,4
5201 - 5550	1,5
5551 - 5950	1,6
5951 - 6300	1,7
6301 - 6800	1,8
6801 - 7200	1,9
7201 - 7600	2,0
7601 - 7950	2,1
7951 - 8350	2,2
8351 - 8700	2,3
8701 - 9050	2,4
9051 - 9350	2,5
9351 - 9700	2,6
9701 - 10050	2,7

(K = kaysers = cm^{-1}.)

On etiam pote usar le formula,

$$\sigma_{vacuo} = (\lambda_{aere} \cdot 1{,}0002706)^{-1},$$

date per W. S. Benedict e E. K. Plyler, J. Research Natl. Bur. Standards, 46, 246 (1951). Iste formula es valide in le region 400 a 18310 K, al minus a 0,1 K.

-- Forrest F. Cleveland e Fred L. Voelz,
Instituto Technologic de Illinois,
Chicago 16, Illinois.

CALENDARIO DE EVENTOS SPECTROSCOPIA

Decembre 10: Symposio super spectroscopia al convention del American Chemical Society, New Orleans, Louisiana, Statos Unite. (Robert T. O'Connor, 2100 Robert E. Lee Boulevard, New Orleans 19, La.)

Junio 14-18: Symposio super spectroscopia e structura molecular, Columbus, Ohio, Statos Unite. (Harald H. Nielsen, Universitate Ohio State, Columbus 10, Ohio.)

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CONTRIBUTIONES FINANCIARI ADDITIONAL

Perkin-Elmer Corporation, Norwalk, Connecticut, Statos Unite; senior Paul A. Wilks, Director Assistente de Venditas e Recerca.

Dr. Eugene Sawicki, Laboratorio de recerca re cancere, Universitate Florida, Gainesville, Florida, Statos Unite.

Costo de un numero de 5 paginas per lector per anno $2.00
Contributiones usque nunc per lector per anno $0.59

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NOVAS E COMMENTOS

(continuate ab pagina 50, columna 2)

NOVE FUNCTIONARIOS DEL Societate pro Spectroscopia Applicate pro le anno 1953-54 es:

Presidente: Van Zandt Williams, Perkin-Elmer Corporation;

Vicepresidente: Paul E. Lighty, Federal Telecommunications Laboratory; e

Secretario: C. A. Jedlicka, United States Testing Company.

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DUO DISCURSOS SPECTROSCOPIC esseva presentate al 14me Conferentia Annual de Recerca del Institutum Divi Thomae Foundation e su affiliates in Cincinnati, Ohio, Septembre 8-11, 1953:

(1) Spectros infrarubie de proteinas in le stato solide: un reporto preliminari, E. B. Barnes, C. W. Kreke, e E. S. Cook;

(2) Le absorption infrarubie e ultraviolette de varie heterocyclos nitrogenose a diamino substituite, Soror Miriam Michael Stimson, Collegio Siena Heights, Adrian, Michigan,

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DEBE NOS HABER UN Societate pro Spectroscopistas Molecular? Vide le discussin in Perkin-Elmer Instrument News. Vol. 4, No. 4.

SPECTROSCOPIA MOLECULAR es publicate mensualmente in interlingua al Laboratorio de Spectroscopia, Instituto Technologic de Illinois, Chicago 16, Illinois, Statos Unite. Illo pote devenir un periodico importante si illo recipe le supporto de spectroscopistas molecular. Manuscriptos in interlingua (o anglese) debe esser submittite a Forrest F. Cleveland al adresse supra-indicate.

Le bulletin se basa super le conviction que illo recipera financiari contributiones voluntari -- sufficiente pro su crescimento e disveloppamento -- ab illes qui beneficia de illo, e ab alteres qui crede que isto es un projecto que merita lor supporto. Le natura e valor de numeros futur essera un mesura del validitate de iste hypothese.

Le texto original es legite per Dr. Alexander Gode, chef del Division de Interlingua de Science Service (80 East 11th Street, New York 3, N.Y.) Libros importante super interlingua es Interlingua-English Dictionary e Interlingua Grammar (Storm Publishers, New York 17).

Labor editorial es gratis. Le costo de preparation e distribution es recipite ab le spectroscopistas, bibliothecas, e companias. Le directores de publication es senioretta Joyce Carol Broling e senior Fred L. Voelz.

. . . . . .

(Posta al adresse supra-date; face cheques pagabile a Forrest F. Cleveland)

☐ Io include $2.00 pro Spectroscopia Molecular pro 1953, e $_____ additional pro le disveloppamento plus rapide de illo.

☐ Io include $2.00 pro Nos. 1-8, 1952.

☐ Io include $0.75 pro Regulas de Selection pro Spectros Vibrational de Moleculas Polyatomic; 1953, 25 paginas.

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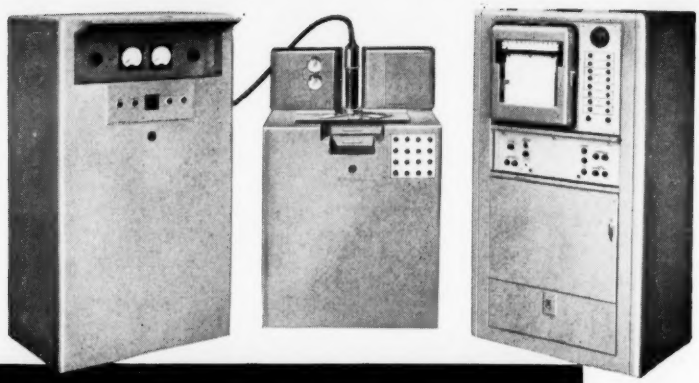

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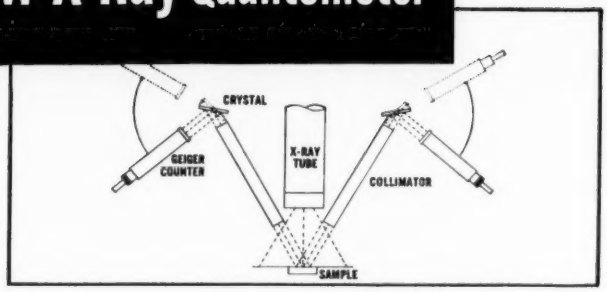

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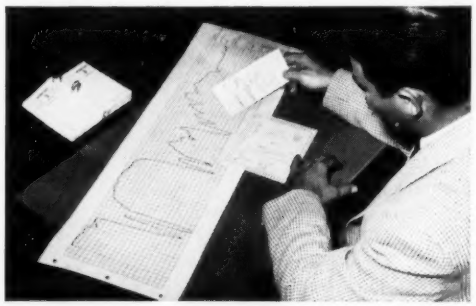

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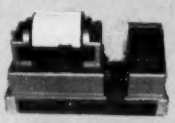

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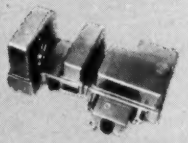

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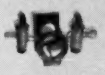
ACCESSORIES:

Demountable Cell—may be assembled to any thickness—for liquids, capillary films, mulls of solids—and films and powders.



Fixed Thickness Liquid Cell—for nearly all liquids and solution work. Standard thickness between 0.025 and 1 mm—others to order.

Standard Gas Cells—2, 5, 10 cm and 1 and 10 m path lengths for various absorption studies.

Microcell—obtains good spectra with 25-100 micrograms—available in thicknesses from 0.025 to 3 mm.

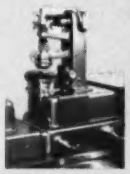
Variable Space Liquid Cell—has accurately variable path length of 0 to 5 mm to bring out features of a spectrum and to compensate for solute absorption in double beam spectrometry.

Reflectance Attachment—for specular reflectance studies of solid materials.

Pressure Cells—for liquids or gasses; path lengths from 0.025 to 50 mm, pressures up to 300 psi. Useful in trace absorption or overtone work. Long and short sizes.

Heating Stage and Heating Stage Power Supply—used with above attachment; permits heating to about 300° C. For studying polymerizations and oxidations. Cycling feature of the Model 21 automatically records reaction stages taking place.

Polarizer—for studies of crystal and molecular orientations. Rotable Cell—To assist in sample orientation for polymerization studies.



Microscope—For analysis of samples of few microns in size as single fibers, tissues, crystals, etc.

Write for Product Bulletin A-3 for more information about these accessories.